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14. ABSTRACT

A series of polyimide resins with low-melt viscosities in the range of 10-30 poise and high glass transition temperatures (T_g's) of 330-370 °C were developed for resin transfer molding (RTM) applications. These polyimide resins were formulated from 2,3,3′,4′-biphenyltetracarboxylic dianhydride (a-BPDA) with 4-phenylethynylphthalic anhydride endcaps along with either 3,4′-oxyaniline (3,4′-ODA), 3,4′-methylenedianiline, (3,4′-MDA) or 3,3′-methylenedianiline (3,3′-MDA). These polyimides had pot lives of 30-60 minutes at 260-280 °C, enabling the successful fabrication of T650-35 carbon fiber reinforced composites via RTM process. Mechanical properties including open hole compression and short beam shear data were collected at room temperature, 288° C and 315 °C were determined. These new resin composites showed excellent retention of properties at 315 °C (600 °F)

15. SUBJECT TERMS

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ABSTRACT

A series of polyimide resins with low-melt viscosities in the range of 10-30 poise and high glass transition temperatures (T_g's) of 330-370 °C were developed for resin transfer molding (RTM) applications. These polyimide resins were formulated from 2,3,3′,4′-biphenyltetracarboxylic dianhydride (a-BPDA) with 4-phenylethynylphthalic anhydride endcaps along with either 3,4′-oxyaniline (3,4′-ODA), 3,4′-methylenedianiline, (3,4′-MDA) or 3,3′-methylenedianiline (3,3′-MDA). These polyimides had pot lives of 30-60 minutes at 260-280 °C, enabling the successful fabrication of T650-35 carbon fiber reinforced composites via RTM process. Mechanical properties including open hole compression and short beam shear data were collected at room temperature, 288° C and 315 °C were determined. These new resin composites showed excellent retention of properties at 315 °C (600 °F)

KEY WORDS: Polyimide, Low-melt Viscosity, High Temperature Composite, RTM370, Resin Transfer Molding, RTM, Biphenyl Dianhydride, a-BPDA

In an effort to develop a simpler and more cost effective way to produce polyimide resins for resin transfer molding (RTM), 2,3,3',4'-biphenyltetracarboxylic dianhydride (a-BPDA), 3,4'-ODA, 3,4'MDA, or 3,3'-MDA and 4-phenylethynylphthalic anhydride (PEPA) could be were mixed and melted to form low viscosity resins terminated with the reactive PEPA endcap. This approach used no solvent in the process and the only volatile generated is water formed during the imidization process. Resins were prepared as outlined below.

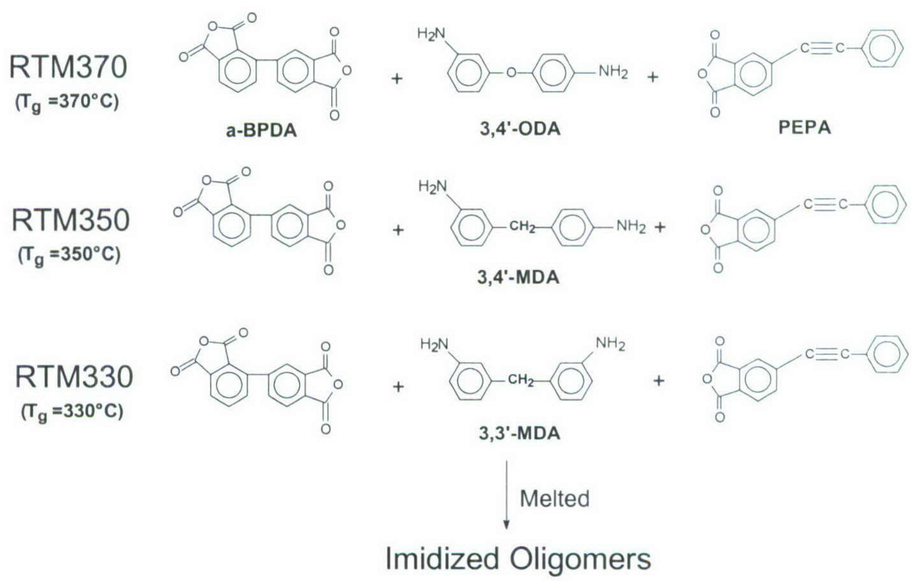

Figure 1: Synthesis of polyimide resins

Sample Synthesis

A mixture of asymmetrical biphenyldianhydride (a-BPDA), 4-phenylethynylphthalic anhydride (PEPA) and the respective diamine was melted above 200 °C for 1 hour to form the corresponding phenylethynyl endcapped polyimide oligomers. The resulting solids were then ground into powders. The absolute viscosities of these imide oligomers were measured using a digital Brookfield viscometer. The rheology was performed in the parallel plate geometry with 1 g of imidized powder at a ramp rate of 4 °C/min and frequency at 100 rad/sec using a TA instruments Ares Rheometer.

Composite Fabrication

Composite panels were fabricated using a high temperature RTM process. The panels were made from T650-35, 8 harness satin weave (8HS) carbon fabrics with an 8 ply quasi-isotropic lay-up $[+45/0/90/-45]_s$. After the tool and the injector were preheated to approximately 288 °C, 600 g of the resin was injected at 1.38 MPa and then cured at 371 °C for 2 hours. The resulting composite panels were post-cured in an oven at 343 °C (650 °F) for 8 hours to achieve the optimal mechanical properties at elevated temperature.

Physical properties and viscosity profiles of neat resins

The imide resins formulated with a-BPDA, 4-phenylethynylphthalic anhydride and either 3,4′-oxydianiline (3,4′-ODA), 3,4′-methylenedianiline (3,4′-MDA) or 3,3′-methylenedianiline (3,3′-MDA), exhibited a post-cured T_g's of 370 °C , 350 °C and 330 °C, respectively (Table 1). Therefore, they are designated as RTM370, RTM350 and RTM330 in reference to their T_g's.

Table 1 Physical Properties of Imide Oligomers/Resins Based on a-BPDA and PEPA

Resin	Diamine	Oligomer Min. η @280 °C by Breookfield [1] (Poise)	Oligomer Min. Complex [η]* @280°C [2] (Poise)	Cured Resin T_g (°C) NPC [3] byTMA	Cured Resin T_g (°C) PC[4]@ 650°F By TMA[5]
RTM370	3,4′-ODA	14	11	342	370
RTM350	3,4′-MDA	7.4	20	338	350
RTM330	3,3′-MDA	1.5	6	288	330

[1] Absolute viscosity measured by Brookfield Viscometer at 280 °C.
[2] Complex viscosity measured by Aries Rheometer, using parallel plates.
[3] NPC = No Post cure
[4] PC = Post cured at 343 °C (650 °F) for 16 hrs.
[5] TMA =Thermal mechanical analysis heated at 10 °C/min, using expansion mode.

At 260-280 °C, these imide resins exhibit a very low-melt viscosities in the range of 2-4 poise that are amenable to RTM, and potentially adaptable to vacuum assisted resin transfer molding (VARTM) processes.

Figure 2 shows that the absolute viscosity of RTM370 and RTM330, as measured with a Brookfield Viscometer at 280 °C, remain steady for 1 hour below 15 and 10 poise, respectively. However, the viscosities of RTM350 drop well below 10 poise initially, but subsequently climb up to 20-30 poise within 30-60 minutes (Figure 2). In practice, a resin viscosity between 10-30 poises with a 1 hour pot-life (reasonable viscosity within processing window) is amenable for

processing by RTM. The rheology profile of RTM370 shows a minimum complex viscosity, $[\eta]^* = 11$ poise, and maintains a viscosity below 30 poise for 20-30 min. (Figure 3). In contrast, RTM350 displays a minimum complex viscosity, $[\eta]^* = 20$ poise, and has a shorter pot-life than RTM370 (Figure 4). The complex viscosities, $[\eta]^*$, measured by parallel plate in a rheometer, are different from the absolute viscosities obtained from the Brookfield viscometer, because they are dependent on the experimental settings in terms of torque and tension and can vary significantly. We have found the rheology experiments conducted at 100 rad/sec allow us to predict composite processing windows.

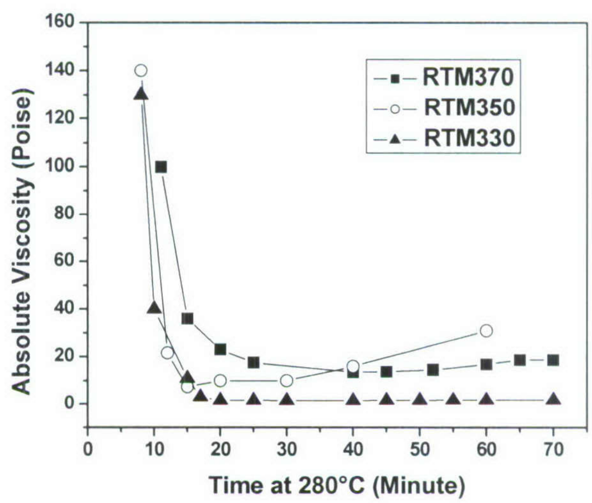

Figure 2: Absolute Viscosities of RTM Resins by Brookfield Viscometer at 280 °C

Table 2 Tg's of Polyimide/T650-35 Composites based on a-BPDA and PEPA

Resin	Diamine	T_g (°C) by DMA[1] NPC [2]	T_g (°C) by DMA PC[3]@ 343°C (650°F)
RTM370	3,4′-ODA	324	356
RTM350	3,4′-MDA	314	337
RTM330	3,3′-MDA	334	361

[1]DMA= Dynamic Mechanical Analysis were performed at 5 °C/min heating rate, using single cantilever.

[2]NPC = No post cure.

[3]PC = Post cured at 343 °C (650 °F) for 8 hours.

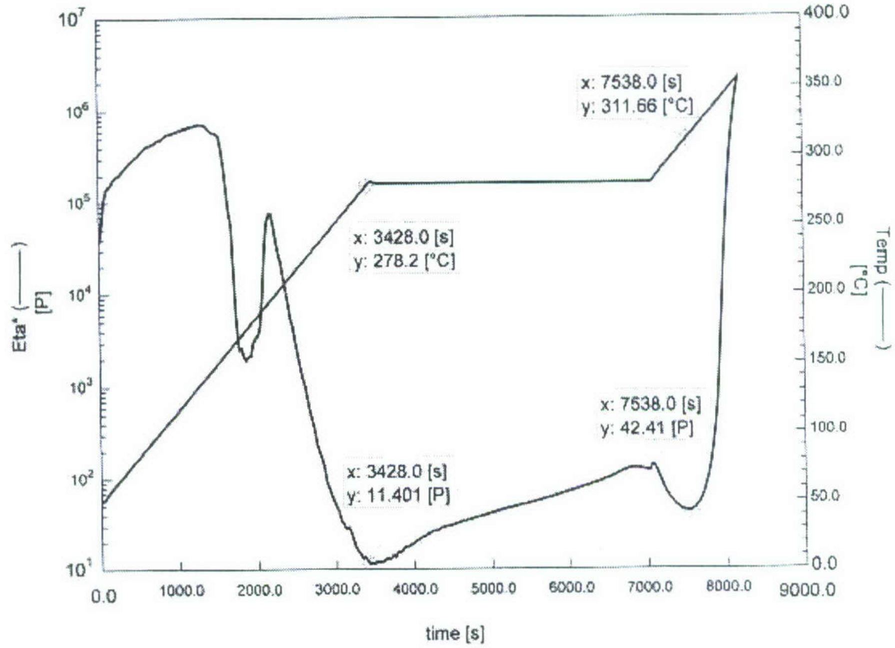

Figure 3: Rheology of RTM 370

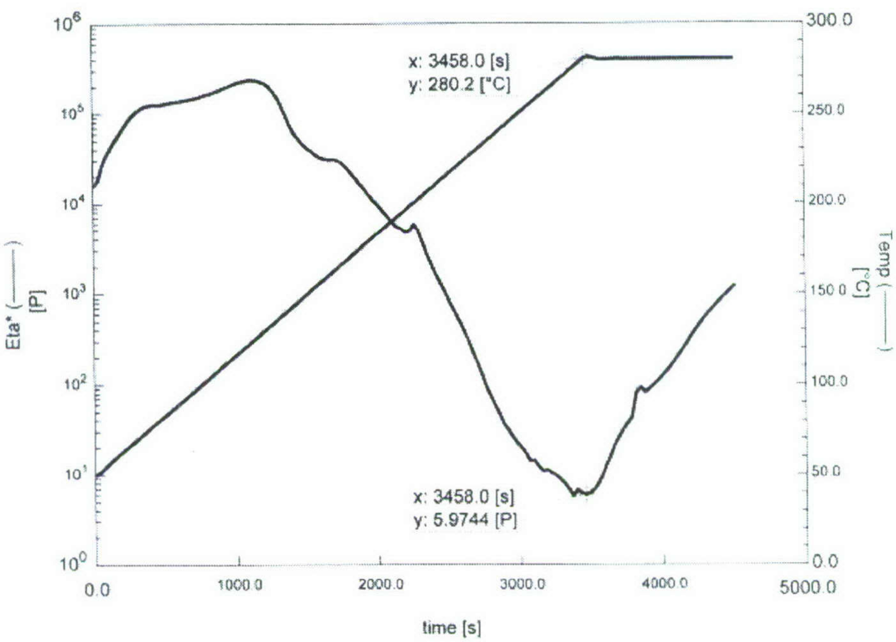

Figure 4: Rheology of RTM330

Characterization and mechanical properties of polyimide/T650-35 composites

T650-35 carbon fabric reinforced composites of RTM370, RTM350 and RTM330 polyimides display T_gs of 356 °C, 337 °C and 361 °C, respectively, after post-cured at 343 °C (650 °F) for 8 hours. (Table 2). The T_g's of RTM370 and RTM350 composites are 15-20 °C lower than those of the corresponding neat resins, but surprisingly the RTM330 composite has a T_g that was 30 °C higher than the corresponding neat resin's. Composites with 60 % fiber volume. Figure 5 show a representative composite panel and figure 6 its C-scan. RTM370 resin has good flow during processing because of its low viscosity and long pot-life, thus the corresponding composite exhibits very uniform resin distribution with no voids as shown in photo micrographs figure 7.

All of the polyimide composites were post cured at 343 °C for 8 hours to achieve optimal mechanical properties before testing. The mechanical properties of composites made from RTM370, RTM350 and RTM330 are compared to the state-of-the-art RTM resin, BMI-5270-1 at ambient and elevated temperatures (Table 3). RTM370 composites exhibit the highest open-hole compressive strength (Figure 8) and modulus (Figure 9) at room temperature among the three resins. However, as the test temperature is increased to 288°C (550°F), all three polyimide composites exhibit similar strength. At 315 °C, RTM350 and RTM330 composites, which contains 3,4′- and 3,3′-MDA isomers respectively, displayed better property retention than the RTM370 composite which is based on 3,4′-ODA. The short beam shear strength of RTM370, RTM350 and RTM330 composites all exhibit very good property retention at 315 °C (Figure 10).

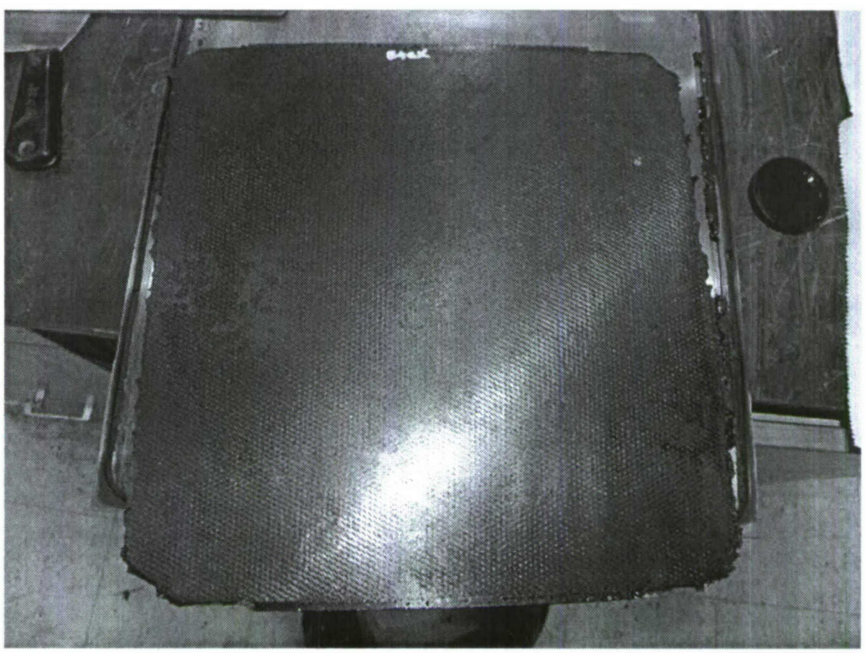

Figure 5 Representative composite panel

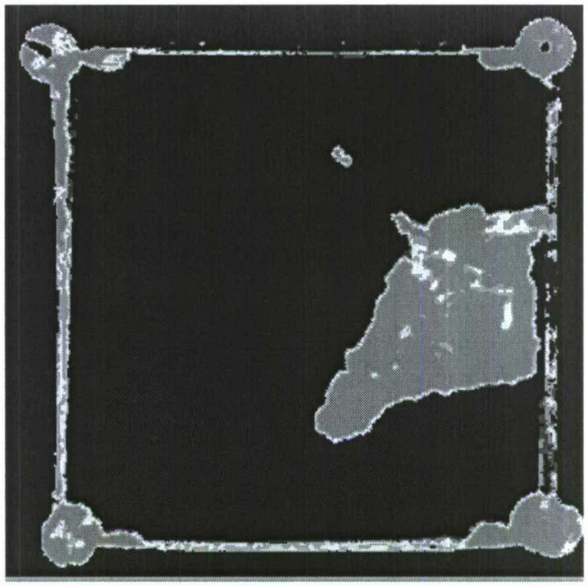

Figure 6: C-scan of a representative panel.

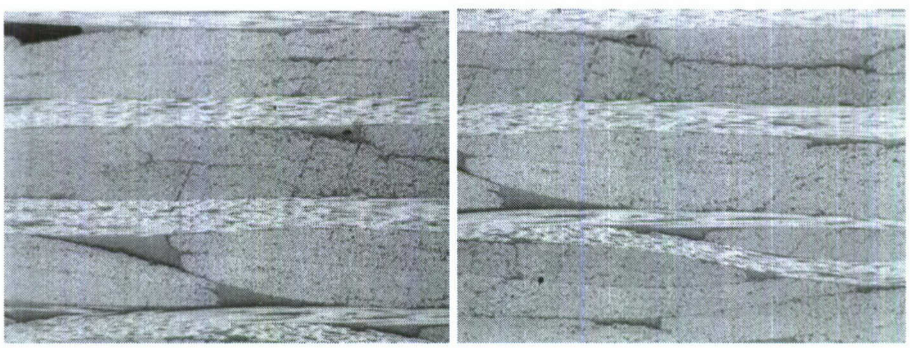

Figure 7: representative photomicrographs

Table 3. Mechanical Properties of RTM370, RTM 350 and RTM330 Compare to BMI-5270-1

Properties	Test Temp. (°C)	RTM 370	RTM 350	RTM330	BMI-5270-1
OHC Strength (MPa)	23	306	285	252	245
	288	223	216	220	148
	315	166	199	185	---
OHC Modulus (GPa)	23	50	43	43	51
	288	47	44	45	38
	315	42	45	50	---
SBS Strength (MPa)	23	62	58	57	37
	288	43	32	38	14
	315	32	31	33	---

OHC = Open-Hole Compression
SBS = Short Beam Shear

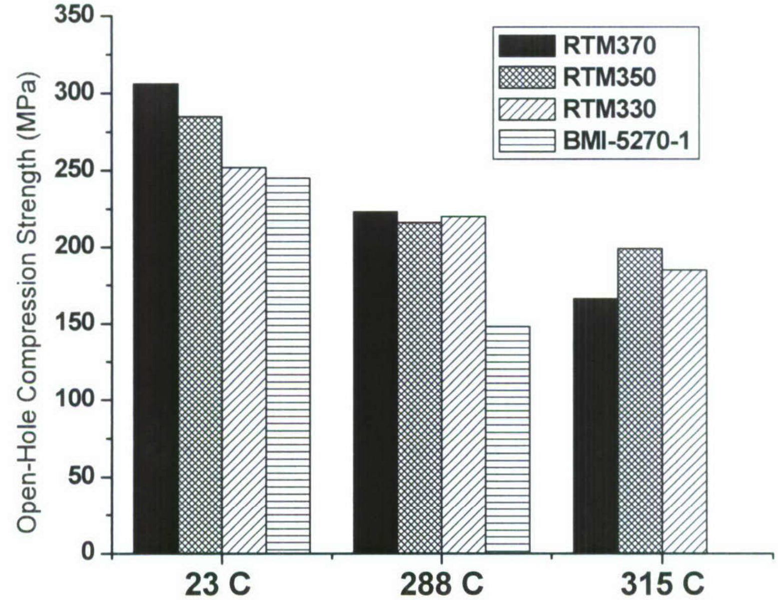

Figure 8: Open-Hole Compression Strength of RTM370, RTM350 and RTM330

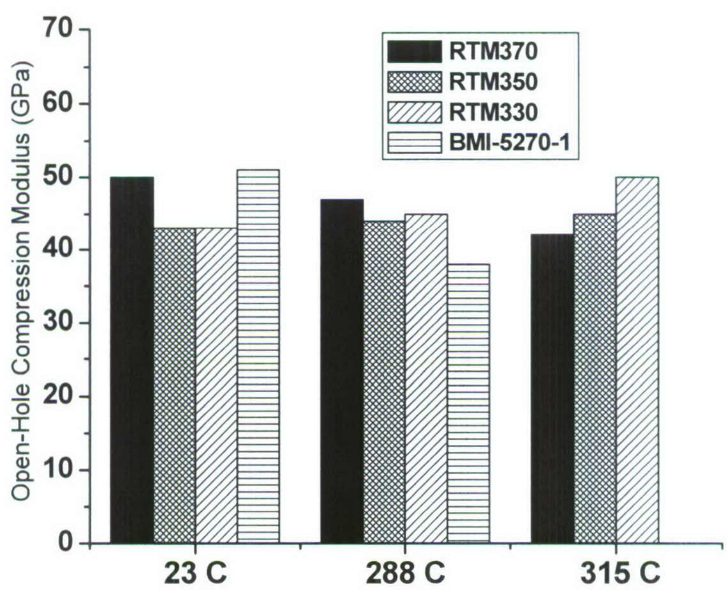

Figure 9: Open-Hole Compression Modulus of RTM370, RTM350 and RTM330

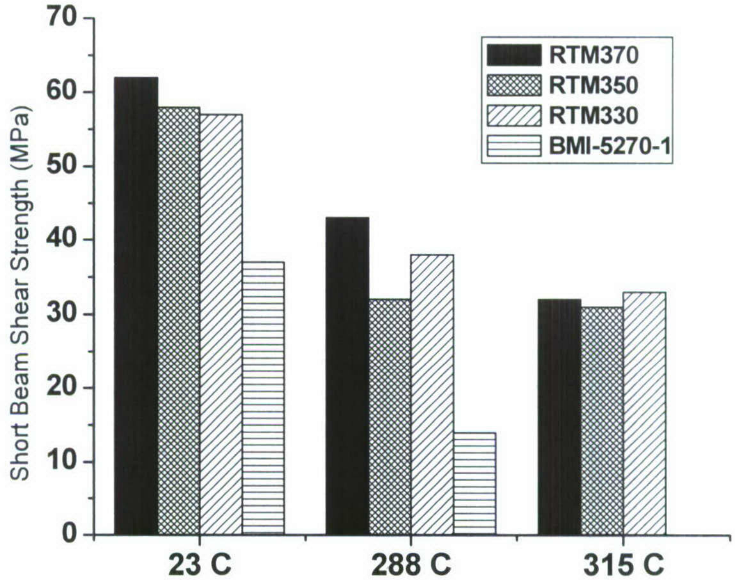

Figure 10: Short Beam Shear Strength of RTM370, RTM350 and RTM330

CONCLUSION

A new series of imide resins (RTM370, RTM350, RTM330) based on 2,3,3′,4′-biphenyltetracarboxylic dianhydride (a-BPDA) and 4-phenylethynylphthalic anhydride (PEPA) endcap, were formulated with either 3,4′-oxydianiline, 3,4′-methylenedianiline or 3,3′-methylenedianiline in a melt, without the use of a solvent. Due to the commercial availability of 3,4′-ODA, RTM370 is cheaper to manufacture than RTM 350 or RTM330. All these resins displayed low-melt viscosities in the range of 10-30 poise at 280 °C with a 1 hour pot-life as measured with a Brookfield viscometer. These resins were successfully injected into T650-35 carbon fabrics by the RTM at 288 °C (550 °F) to produce composites with high fiber volume and low void volumes. The elimination of organic solvents involved in the preparation of the imide oligomers by a simple melt process reduces the resin cost. RTM370, RTM350 and RTM330 all exhibited excellent open-hole compressive strength and modulus, and retained about 75% of their room temperature properties at 288 °C (550 °F). In addition, RTM370, RTM350 and RTM330 maintained 65-70% of their room temperature short beam shear strength at 288 °C. Most importantly, due to their high T_g's, RTM370, RTM350 and RTM330 all exhibit outstanding property retention 315 °C (600 °F), exceeding state-of-the-art RTM resins, such as BMI-5270-1. These resins offer the potential of producing high temperature composites at significantly reduced cost by a) eliminating the solvent during resin synthesis and fabrication, and b) enabling the use of cost effective manufacturing methods, such as resin transfer molding (RTM) and resin infusion (RI).